

Studies on Solid Catalysts with a Basic Character

II. Nature of Acidic and Basic Centers on the Surface of Sodium-Silica Catalysts

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The surface properties of silica impregnated with varying sodium amounts have been investigated. Specific surface, pore volume, and mean pore radius were determined. Water content in, and infrared spectra of the water molecules bonded to the catalysts were studied. Adsorption was investigated of γ -picoline, pyridine, ammonia on the surfaces of the catalysts.

Consistency of the observed ammonia adsorption with Langmuir's and Temkin's adsorption isotherms was examined. Adsorption rate of ammonia and its agreement with the Elovich kinetic equation was studied. The heat of adsorption and the maximum number of ammonia adsorption centers were calculated. The quantities determined were investigated as functions of the amount of milligram-ions of Na^+ per square meter of catalyst surface area, experimental temperature, and catalyst degassing temperature. As the sodium content in the silica surface was increased, adsorption of the pyridine bases, ammonia, and carbon dioxide rose.

The investigations of the silica catalysts containing various amounts of Na^+ ions were described in the preceding paper (1). The acid-base properties of the surface as determined by the adsorption of indicators from nonpolar solutions and by the potentiometric titration of the catalysts suspended in acid or basic media allowed to infer that the surface of each catalyst investigated simultaneously contains acidic and basic centers.

As a working hypothesis, the groupings, $\begin{array}{c} | \\ \text{—Si—ONa} \\ | \end{array}$ were assumed to be the basic active centers. Their number is directly related to the amount of sodium deposited on the gel. On the other hand, the number, structure and distribution of acidic centers continue to remain either obscure or controversial. Numerous investigations have been reported, devoted to the elucidation of the structure of acidic centers on the surfaces of various dried gels, particularly silica, aluminum, and

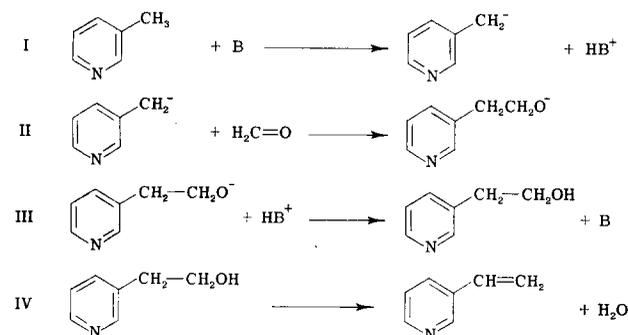
aluminum-silica. But the deposition of the alkali metals distorts the surface pattern and the structure and distribution of active centers.

The purpose of the present investigations is to study the surface properties of silicas with varying amounts of sodium ions deposited thereon.

Sodium-impregnated silicas are used as basic catalysts in aldolic condensations carried out in heterogeneous gas-solid systems. The studies on the mechanism of the acetaldehyde-formaldehyde condensation to acrolein, treated as a model reaction (2), showed the rate constant to be proportional to the amount of sodium ions on the catalyst surface. On this basis the catalysis was assumed to be basic in nature and —Si—ONa groupings were suggested to be the active centers. These data (2) and the studies of aldolic condensations in homogeneous systems (3) prompted the authors to investigate the condensation of picolines with formaldehyde to vinyl pyridine in the presence of

silica catalysts with the surfaces impregnated by varying amounts of alkali metal hydroxides.

With α - or γ -picoline as the mobile-hydrogen compound, the condensation with formaldehyde in the presence of solid basic catalysts was assumed to proceed by the following mechanism:



Collectively:



where B is the basic center.

The equilibrium conditions, established by the van Krevelen method, showed the process to be thermodynamically favored, the equilibrium yields exceeding 90%. The data calculated are presented graphically as a function of temperature in Figs. 1 and 2.

Attempts to condense α - and γ -picolines with formaldehyde in the gas phase over silica catalysts containing various amounts of sodium ions on the surface, failed. Therefore sodium was replaced by more alkaline metals, viz., potassium, rubidium, and cesium, and various reactant mole ratios were used. The reaction was carried out at temperatures of 150° to 500°C and flow rates of 7–30 ml/hr. Gas chromatography revealed the absence of vinyl pyridine or products of its further condensation in the reaction mixture.

These failures instigated a study of the acid-base properties of the sodium-silica catalyst surface, because it was felt that acidic centers on the surface obstructed the process in the gas phase.

The following assumptions were made: The picoline molecule endowed with two centers of opposite properties can combine through nitrogen with acidic centers on the catalyst surface, whereby interactions between the mobile hydrogen of the methyl group and basic centers on the surface are rendered difficult. In this manner Step I

of the above mechanism is obstructed and the consecutive reactions become impossible.

EXPERIMENTAL

Catalysts. Granulated silica was impregnated with identical volumes of sodium hydroxide solutions of varying concentrations to obtain seven catalysts differing in the amount of sodium ions on the surface:

No.	Na ⁺ × 10 ⁻³ , mg-ions/m ²
1	0.00
2	0.79
3	1.49
4	2.54
5	4.57
6	9.26
7	22.70

Specific surface was evaluated from the BET nitrogen adsorption isotherms.

Pore volume and mean pore radius were determined by the helium-mercury method.

* In certain studies a 14.6 × 10⁻³ mg-ions Na⁺/m² catalyst also was employed.

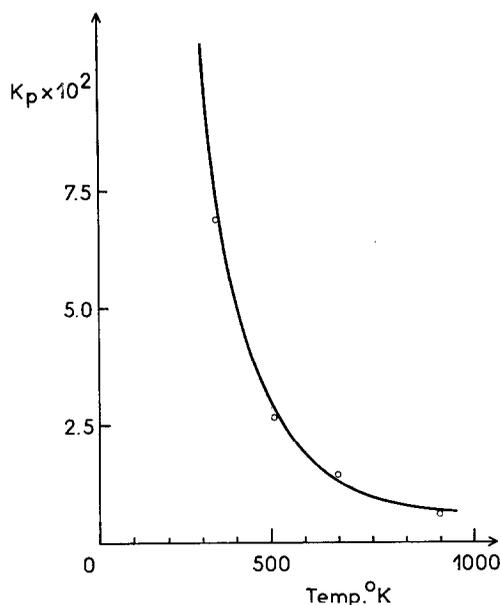


FIG. 1. The chemical equilibrium constant for the condensation of picolines with formaldehyde to vinyl pyridine as a function of absolute temperature.

Water/mmoles/m² was determined in the catalysts predried for 48 hr at 120°C and barometric pressure and in those degassed for 10 hr at 300°C and 10⁻² mm Hg. Weighed catalysts specimens were ignited to constant weight in a muffle furnace at

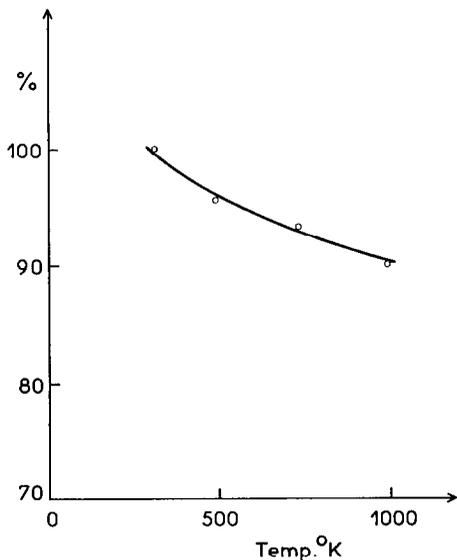


FIG. 2. The theoretical yield of vinyl pyridine in equilibrium conditions as a function of absolute temperature.

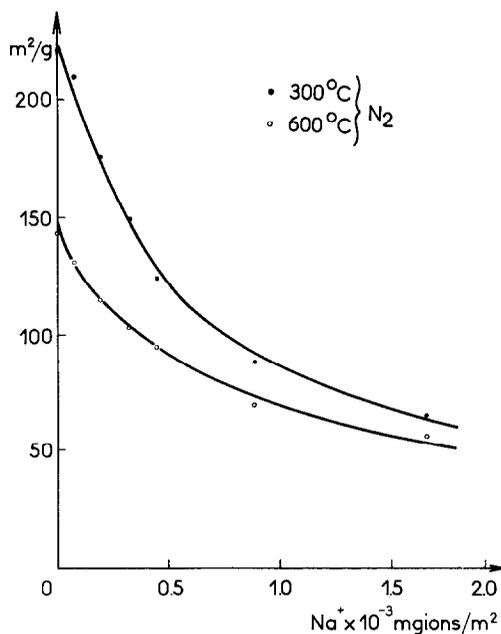


FIG. 3. The specific surface as a function of mg ions Na⁺/g catalyst degassed at 300° and 600°C.

at 1300°C and water was established by difference.

Infrared spectra were run with a Unicam FP 200 spectrophotometer on the catalysts

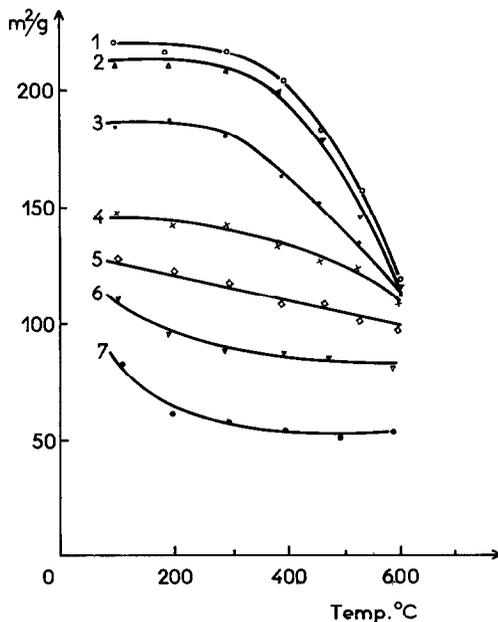


FIG. 4. The specific surface as a function of the temperature of degassing of catalysts with varying sodium contents.

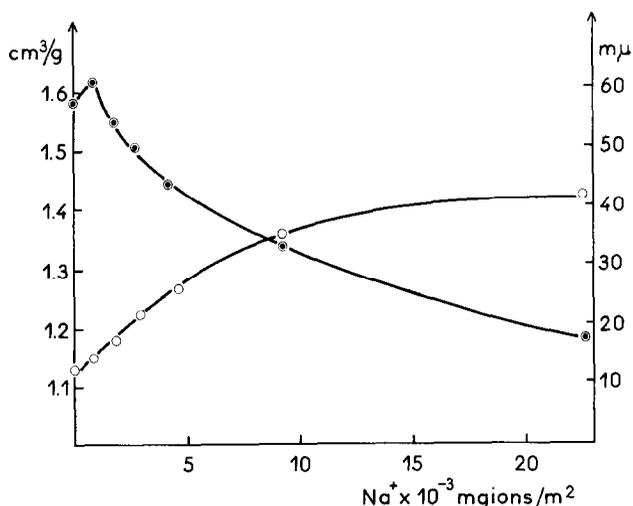


FIG. 5. The pore volume and the mean pore radius as functions of mg-ions Na^+/m^2 catalyst surface.

mulled with hexachlorobutadiene and applied in ≈ 0.3 -mm films to potassium bromide disks. The spectra are recorded as the percentage absorption against wavenumber.

Adsorption of γ -picoline and pyridine was studied in a BET apparatus thermostated at 100°C and the adsorbate was recalculated as the number of molecules per square meter.

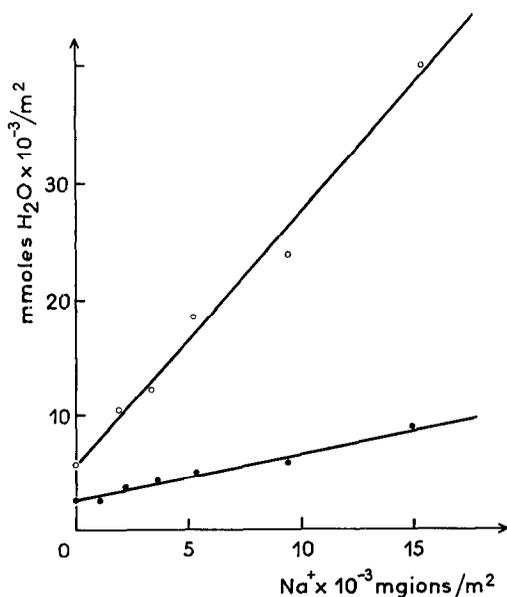


FIG. 6. Water in the catalyst as a function of mg-ions Na^+/m^2 catalyst surface.

Adsorption of ammonia and carbon dioxide was studied in a conventional BET apparatus at 20°C . The apparatus was equipped with seven quartz cells, which enabled seven catalysts examined to be simultaneously degassed in identical conditions. The catalysts to be studied in adsorption at temperatures up to 300°C were degassed for 3 hr at 6×10^{-5} mm Hg. For still higher adsorption temperatures the specimens were degassed at the measurement temperatures. Adsorption of ammonia and carbon dioxide was investigated at pressures of 80–200 mm Hg and temperatures of -23° – 600°C and the adsorb-

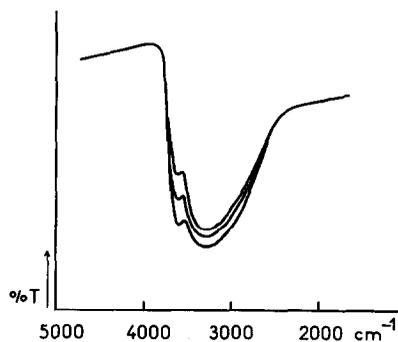


FIG. 7. Infrared absorption spectra of three catalysts: (1) sodium-deficient catalyst; (2) 4.57×10^{-3} mg-ions Na^+/m^2 catalyst and (3) 22.7×10^{-3} mg-ions Na^+/m^2 catalyst preheated at 200°C and 10^{-2} mm Hg.

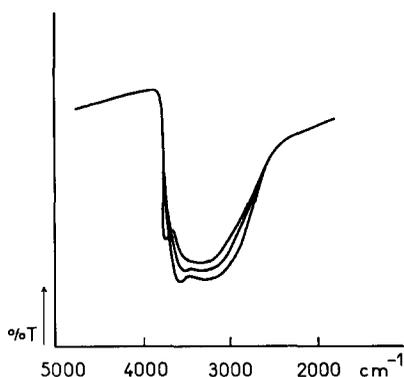


FIG. 8. Infrared absorption spectra of three catalysts: (1) sodium-deficient catalyst (2) a 4.57×10^{-3} mg-ions Na^+/m^2 gel; and (3) a 22.7×10^{-3} mg-ions Na^+/m^2 preheated at 400°C and 10^{-5} mm Hg

ates were converted into the number of molecules per square meter.

RESULTS AND DISCUSSION

The physical properties of the silica catalyst surfaces impregnated with various amounts of sodium hydroxide and dried in vacuum at various temperatures change distinctly with the sodium content and drying temperature. For the catalysts degassed at 300° and 600°C the specific surface is plotted in Fig. 3 as a function of sodium content. For the catalysts differing in sodium content the specific surface is presented as a function of the degassing temperature (Fig. 4). The surface diminishes as the sodium content or the degassing temperature is increased. High-sodium catalysts are less sensitive to the degassing temperature, but in sodium-deficient or sodium-poor catalysts the surface diminishes rapidly as the degassing temperature is raised.

Pore volume and mean pore radius are shown in Fig. 5 as a function of sodium content per unit surface area. As the sodium content is increased, the pore volume diminishes and the mean pore radius increases. These data point to structural changes in the catalyst associated with a progressive vitrification of the surface.

The surface structure and catalytic activity are, particularly for reactions of ionic mechanisms, highly affected by the molecules of water bonded to the catalyst.

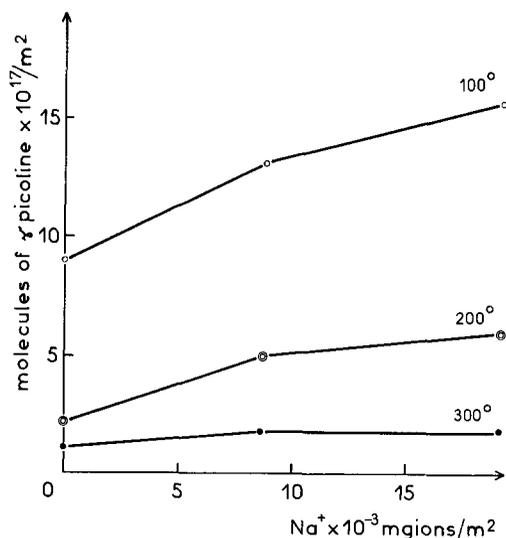


FIG. 9. The number of γ -picoline molecules adsorbed at three temperatures on the catalyst surface as a function of mg-ions Na^+/m^2 .

The present catalysts were assumed to contain: the constitution water in the form of free OH groups, the hydration water introduced during the preparation, and the water adsorbed on the surface. Water contents in the specimens dried at 120°C and barometric pressure and in ones dehydrated in vacuum at 400°C , plotted against

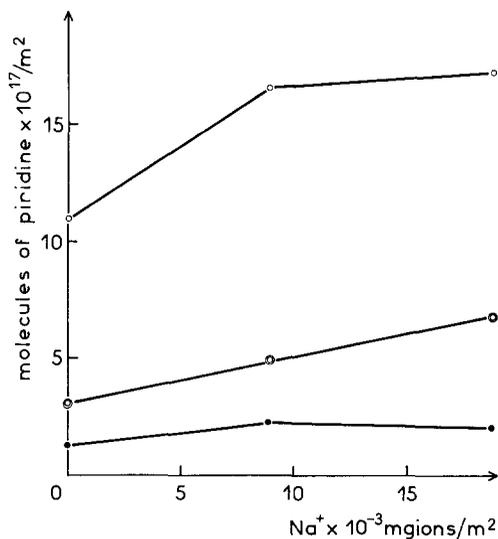


FIG. 10. The number of pyridine molecules adsorbed at three temperatures on the catalyst surface as a function of mg-ions Na^+/m^2 .

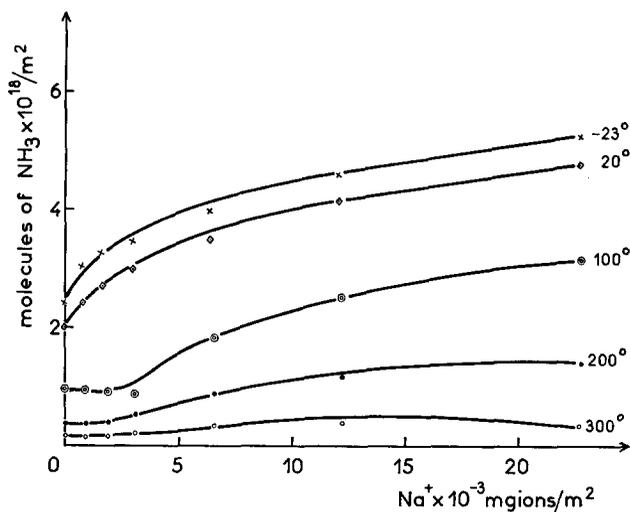
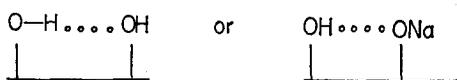


FIG. 11. The number of NH_3 molecules/ m^2 adsorbed at various temperatures as a function of mg-ions Na^+/m^2 . The catalysts were degassed at 300°C .

sodium content per unit surface area (Fig. 6), follow straight-line courses and increase as the sodium content is raised.

The spectral studies were carried out with the samples with zero, medium, and maximum sodium contents (Nos. 1, 5, and 7). The spectra were recorded for the specimens degassed at 200°C and 2×10^{-2} mm Hg (Fig. 7) and for those degassed at 400°C and 10^{-5} mm Hg (Fig. 8). The former spectra, examined at wavenumbers of $5000\text{--}2000\text{ cm}^{-1}$, exhibit two absorption bands: a narrow band at 3650 cm^{-1} and a broad band at 3400 cm^{-1} . The spectra are almost identical for all three specimens, except for the intensity of the narrow and the broad bands. The 3650-cm^{-1} band is attributable to valence vibrations of free OH groups. It is shifted towards longer wavelengths, which is suggestive of some attenuation of the oxygen-hydrogen bond in the OH group. This may well be caused by interactions of the adjacent OH or the OH and ONa groups on the surface.



Naccache's studies (4) confirmed this phenomenon.

The 400°C specimen spectra also exhibit two absorption bands; the broad 3400-cm^{-1}

band occurs in each spectrum regardless of catalyst dehydration conditions and is assigned by most investigators to hydrogen-bonded OH groups. As the dehydration temperature and vacuum are increased, the narrow bands become more and more shifted. The sodium-deficient preparation exhibits a narrow band at 3760 cm^{-1} corresponding exactly to valence vibrations of free OH groups. This would indicate that the bonds between the adjacent OH groups are ruptured, as also confirmed by Naccache's data. However, with the sodium-impregnated samples the narrow band is shifted towards longer wavelengths, a fact suggestive of strengthening of bonds between the surface OH and ONa groups and thus of weakening of the oxygen-hydrogen bond in the OH group. The increase in the intensity of both the narrow and the broad bands with rise in the surface sodium content points to an increase in the number of free and hydrogen-bonded OH groups.

The spectral studies indicate also that, as the catalyst degassing temperature is increased, the polarizing action of surface ONa on surface OH groups rises in strength.

On the basis of earlier data (1, 2) the sodium-silica catalysts were assumed to be amphoteric in nature and the basic cen-

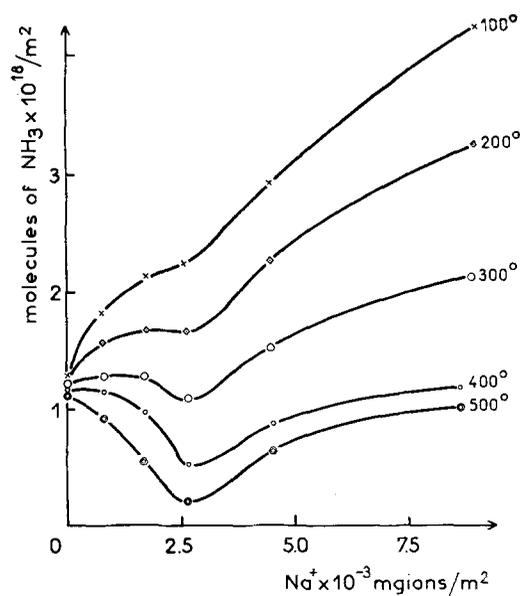


FIG. 12. The number of NH_3 molecules/ m^2 adsorbed at 100°C as a function of mg -ions Na^+/m^2 . The catalysts were degassed at various temperatures.

ters on the surface to increase in number with rise in sodium content; the surface

— Si — ONa groups are basic active centers.

The studies of gas-phase condensations of α - and γ -picolines with formaldehyde over the sodium-silica catalysts led to another assumption, viz., that picoline molecules having two centers opposite in properties can be bonded to the surface via combination of either the hydrogen of the methyl group or the electron pair on the nitrogen with basic and acidic surface centers, respectively.

Preliminary studies were carried out of adsorption of γ -picoline and pyridine vapor in the conditions closely approaching those of the catalytic process to reveal how the picoline molecules combine with the surface of the sodium-silica catalysts. If these molecules are adsorbed on basic centers, the adsorption curves of γ -picoline and pyridine plotted as functions of mg -ions of Na^+ per unit surface area of the catalyst should follow markedly different courses. The curves obtained (Figs. 9, 10) show that the adsorption increases as the sodium content is raised. Furthermore, in strictly

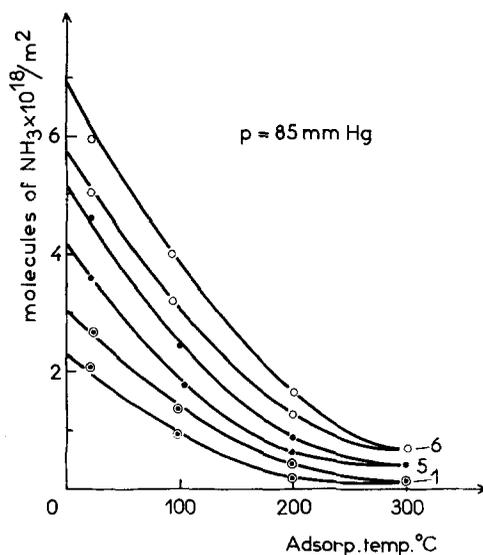


FIG. 13. The number of adsorbed ammonia molecules/ m^2 as a function of experimental temperature up to 300°C .

similar conditions the γ -picoline and the pyridine molecules adsorbed are close in number. These facts are indicative of the same type of adsorption, viz., adsorption on acidic centers of the surface.

At the same time the highest adsorption was found to occur on the catalysts containing large amounts of Na^+ ions, larger than those demanded to neutralize all the surface OH groups. For investigation of this paradoxical phenomenon in more detail, gaseous ammonia was adsorbed on the surfaces of catalysts of varying sodium contents.

The number of ammonia molecules adsorbed at a fixed pressure of 85 mm Hg and varying temperatures on the surfaces of catalysts degassed at 300°C and 6×10^{-5} mm Hg is plotted in Fig. 11 as a function of the amount of mg -ions of Na^+ per square meter of the catalyst surface area. In each case the adsorption of ammonia rises with increase in sodium content. A similar relationship studied at a single temperature of 100°C and ammonia gas pressure of 200 mm Hg on the catalysts degassed at various temperatures is presented in Fig. 12. The data obtained are difficult to interpret because, as the number of basic centers on the catalyst surface in-

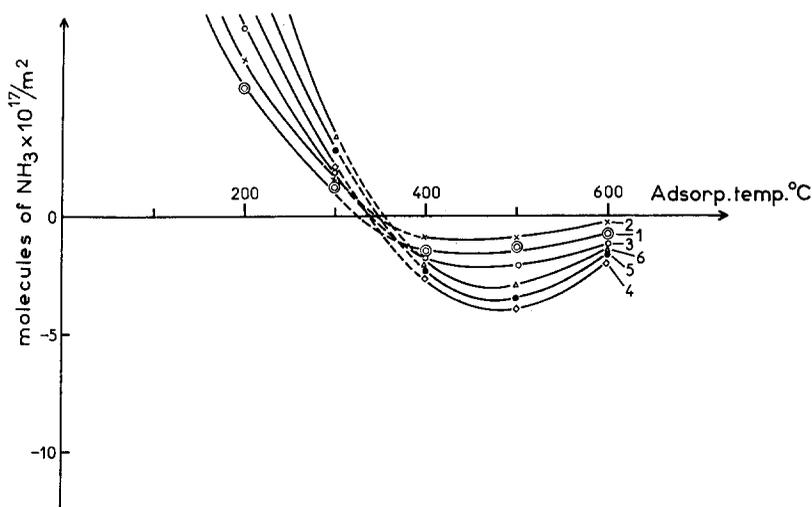


FIG. 14. The number of adsorbed NH_3 molecules/ m^2 as a function of experimental temperature above 300°C .

creases, the adsorption of molecules also possessing basic properties does likewise. This fact indicates that impregnation of the silica surface with sodium hydroxide results not only in production of basic centers but also in formation of new acidic centers. Confirmatory to this suggestion are Sato's data (5) on the number of OH groups, as determined by reaction with organoaluminum compounds, on the surfaces of pure and sodium-poisoned alumina, silica, and alumina-silica catalysts. With each catalyst more OH groups were found to occur on the poisoned than on the unpoisoned surface. This fact was explained in terms of a Na^+ ion-effected cleavage of bonds between silicon or aluminum and oxygen atoms and subsequent formation of $-\text{Si}-\text{ONa}$ and $-\text{Si}-\text{OH}$ or $-\text{Al}-\text{ONa}$ and $-\text{Al}-\text{OH}$ groupings.

While studying the role of OH groups on the surface of typical acidic catalysts such as alumina-silica and zirconia-silica, Ignateva (6) showed that, after acidic centers have been poisoned with sodium or lithium hydroxide, the catalytic activity diminishes but the number of OH groups remains unaffected. Furthermore, infrared spectra of pyridine adsorbed on the alkali-

poisoned and unpoisoned catalysts revealed characteristic changes indicative of formation of hydrogen bonds between OH groups and pyridine.

Imelik and co-workers (7) demonstrated that dehydration of formic acid in the presence of silica occurs with the participation of the hydrogens of surface hydroxyl groups of the catalyst. Addition of alkali metal ions to the silica was found to enhance its catalytic activity.

The data referred to support our suggestion that protonic acidity centers are formed on the surface of silica during impregnation by sodium ions.

The adsorption and desorption of ammonia is presented in Fig. 13 as a function of temperature. The number of adsorbed ammonia molecules decreases as the adsorption temperature is increased. Above 300°C , this number rises (Fig. 14); studies of this phenomenon will be described in a forthcoming communication.

The water content data, infrared spectra and the results of other investigators indicate that adsorption of the nitrogen bases on the surfaces of the catalysts examined is primarily affected by the water molecules bonded to the surface either as the constitution water in the form of OH groups or as adsorbed water. The present data show that the amount of water com-

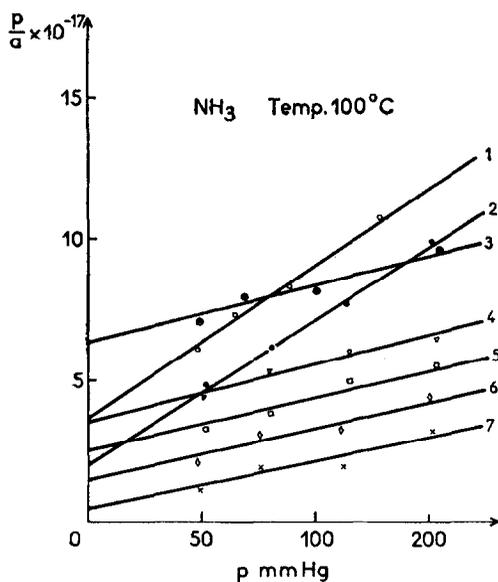


FIG. 15

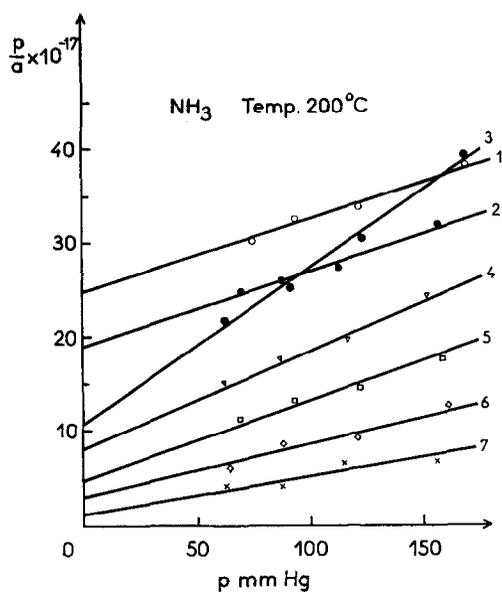


FIG. 16.

FIGS. 15, 16. The ammonia adsorption isotherms Langmuir's function: p/a vs. p .

combined with the catalyst and the strength of bonds between the water molecules and the catalyst surface increase as the sodium content is raised. Adsorption of the nitrogen bases also rises. The water molecules strongly bonded to the surface owing to the polarizing action of surface basic

groups can afford centers of high protonic acidity, and at the same time centers of adsorption for ammonia and pyridine bases, on the surface of the sodium-silica catalysts.

Since the literature furnishes too few experimental data to permit an unequivocal interpretation of the above relationships, further studies were carried out on adsorption of ammonia to shed more light on the nature of the acidic centers on this type of catalysts.

Ammonia was adsorbed at low temperatures at which physical adsorption prevails and at temperatures at which catalytic affects occur and chemical adsorption predominates. Within the temperature range 20° – 300° C adsorption of the mixed type was assumed to occur. The data were fitted to the Langmuir (8) isotherm equation

$$\frac{p}{a} = \frac{1}{a_m \lambda} + \frac{p}{a_m}$$

where a is the number of molecules adsorbed per square meter; a_m , the number of molecules adsorbed per square meter at saturation; p , the gas pressure; and λ , Langmuir's coefficient of adsorption. According to the equation, the p/s ratio should be a linear function of pressure p . Adsorption of ammonia on silica catalysts with varying sodium contents was investigated at four temperatures (Figs. 15, 16). In each case the Langmuir isotherm equation was a fairly good fit. In each temperature the family of straight lines, each line corresponding to the given sodium content, follows a different course. These differences are associated with the quantities a_m and λ . The former quantity defines the maximum number of adsorption centers, in this case for adsorption of ammonia. The latter quantity is a logarithmic function of the energy of adsorption. Both were evaluated by the least-squares method.

The maximum number of ammonia adsorption centers is plotted against the amount of Na^+ mg-ions per square meter of the catalyst surface area in Fig. 17 and against the experimental temperature in

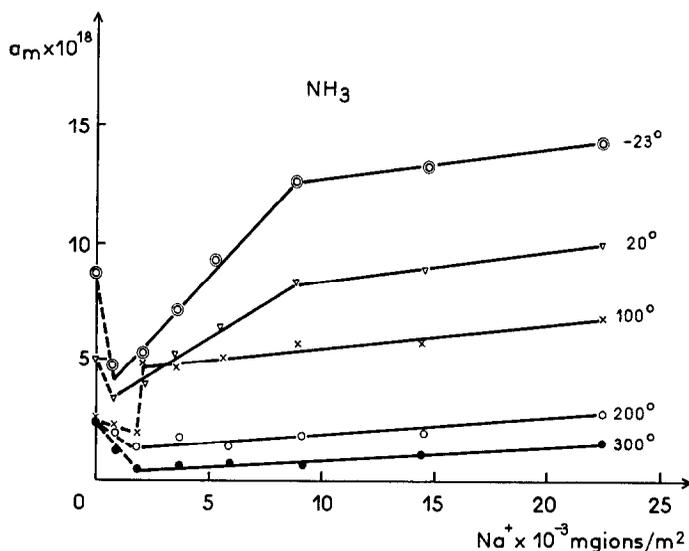


Fig. 17. The maximum number of NH_3 adsorption centers/ m^2 as a function of $\text{mg-ions Na}^+/\text{m}^2$.

Fig. 18. The two plots show that a_m increases as the sodium content in the catalyst surface is raised, and diminishes as the adsorption temperature is elevated. At low sodium content a_m varies in a stepwise manner. This phenomenon is not infrequent. While studying various physico-chemical properties of mixed catalysts as a function of the content of a single component, numerous investigators recorded stepwise changes within the range of low extraneous

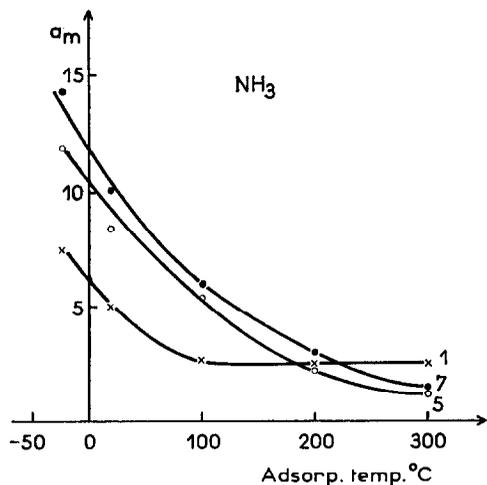


Fig. 18. The maximum number of NH_3 adsorption centers/ m^2 as a function of adsorption temperature.

ion concentrations. Uytterhoeven, Sleex and Fripiat (9) explored the surface properties of silicas and found that there exists a well-defined Na^+ ion concentration, viz., 5×10^{-4} $\text{mg-ions}/\text{m}^2$, above which the structure of the silica catalyst undergoes rapid changes. In the present investigations stepwise changes were found to occur within the region $0.5-1.5 \times 10^{-3}$ $\text{mg-ions Na}^+/\text{m}^2$.

By using the equation $\lambda = \lambda_0 \exp(Q/RT)$ and the λ -coefficients determined at varying temperatures, the heat of adsorption (Q) of ammonia was evaluated for specimens of different sodium content. Since the function $\ln \lambda = f(T)$ proved to be nonlinear, the λ_0 values were estimated from the following relationship:

$$\lambda_0 = N\tau_0\delta^0(2RTM)^{-0.5}$$

where:

- δ^0 = the surface area occupied by a single ammonia molecule,
- τ_0 = the oscillation time for a single molecule,
- M = the molecular weight of ammonia,
- R = the gas constant,
- T = the absolute temperature, $^\circ\text{K}$

The heats of adsorption are presented in Fig. 19 as a function of the number of

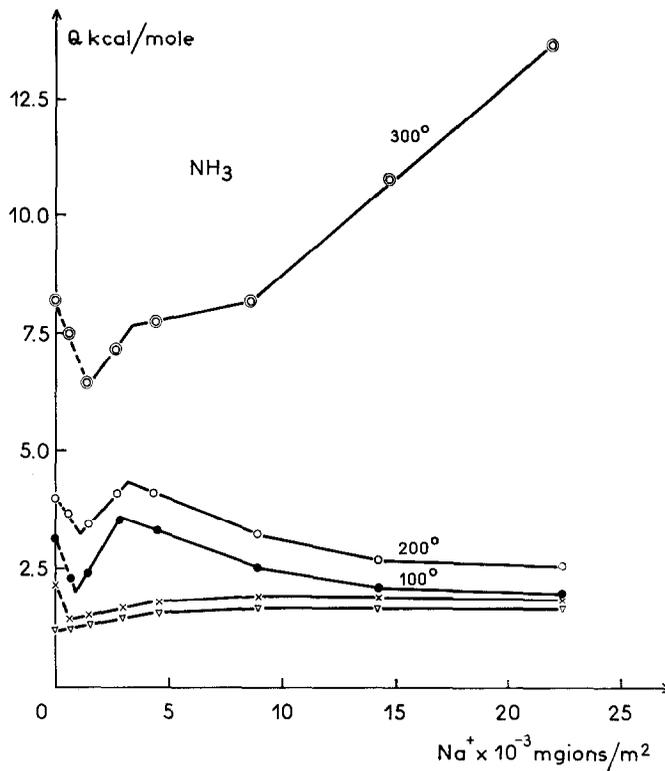


FIG. 19. The isosteric heat of ammonia adsorption as a function of mg-ions Na^+/m^2 .

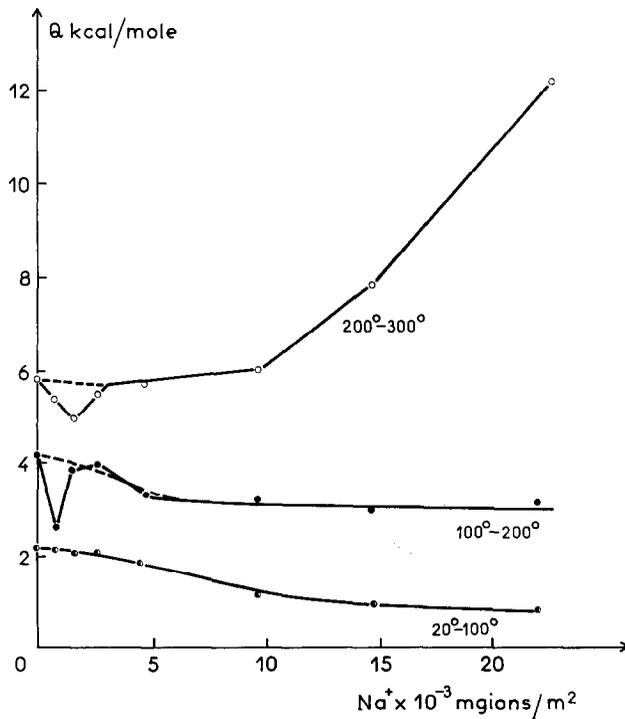


FIG. 20. The isosteric heats of ammonia adsorption as a function of mg-ions Na^+/m^2 .

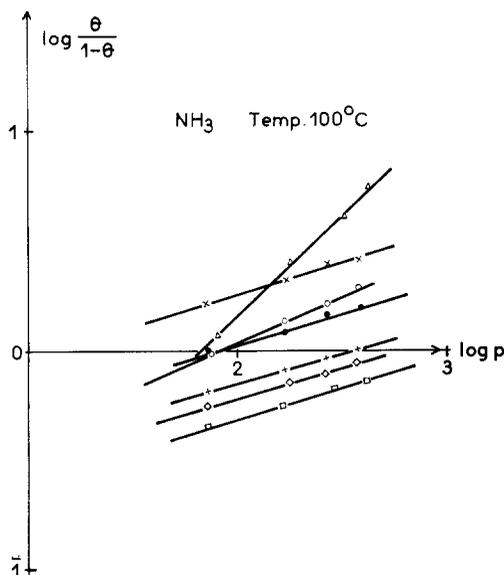


FIG. 21. The ammonia adsorption isotherms Temkin's function $(\theta/1 - \theta)$ vs. p .

mg-ions of Na^+ per square meter. The data indicate that the heat of adsorption varies with temperature, contrary to Langmuir's assumptions. Therefore, isosteric heats of adsorption (Fig. 20) were calculated from the Clausius-Clapeyron equation $d \ln(p/dT) = -\Delta(H/RT^2)$. Despite the Langmuir adsorption isotherm's being a good fit (presumably accidental) to the adsorption of ammonia on sodium-impregnated silica catalysts, neither the heat of adsorption nor the adsorption centers can be assumed constant and uniform, respectively. Consistency was therefore explored with Temkin's adsorption isotherm

$$\lambda_0 p = \frac{\theta}{1 - \theta} \exp(\gamma \rho)$$

or, upon taking logarithms,

$$\frac{1}{\gamma} \ln \lambda_0 p = \frac{1}{\gamma} \ln \frac{\theta}{1 - \theta} + \theta$$

where:

- θ = the fraction of surface coverage
- p = pressure
- λ_0 and γ = constants.

In the Temkin isotherm equation, adsorption centers are assumed to be non-

homogeneous and the heat of adsorption is allowed to vary with temperature and surface coverage fraction.

In the present investigations a simplified form of the Temkin equation was used, viz.,

$$\theta = \frac{1}{\gamma} \log \lambda_0 + \frac{1}{\gamma} \log p$$

i.e., the $1/\gamma \ln \theta(1 - \theta)$ term was assumed to be negligibly small. As is evident from Figs. 21, 22, Temkin's isotherm is a very good fit. The heats of adsorption were calculated from the ΔE vs. $-\gamma RT \theta$ plots and found to be very close to the previous values, except they are variable with changes in surface coverage fraction effected by varying ammonia pressures. The differences reach up to 1.8 kcal/mole.

The data were statistically analyzed in terms of sums of the squares of relative deviations of experimental points from the least-squares lines evaluated for Langmuir and Temkin isotherms. These deviations calculated for various catalysts and various temperatures are listed in Table 1. They are very low for each isotherm, but with catalysts containing more than 1.42 mg sodium, Temkin's isotherm shows a closer fit.

With due consideration given to the

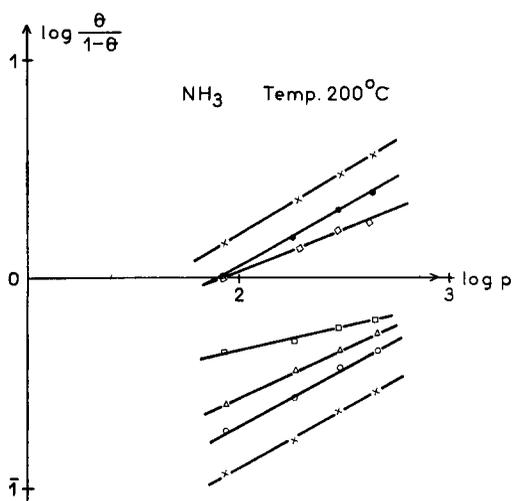


FIG. 22. The ammonia adsorption isotherms Temkin's function $(\theta/1 - \theta)$ vs. p .

TABLE 1
SUMS OF THE SQUARES OF RELATIVE DEVIATIONS

$$\sum \left(\frac{y - y'}{y} \right)^2$$

y = values calculated; y' = values experimental

	No. of catalyst (temp. of adsorption, 0°C)						
	1	2	3	4	5	6	7
Isotherm of Langmuir							
100°	2.66×10^{-2}	5.82×10^{-3}	3.14×10^{-2}	9.10×10^{-2}	3.76×10^{-3}	1.27×10^{-3}	7.96×10^{-3}
200°	3.37×10^{-1}	3.20×10^{-2}	8.91×10^{-2}	2.86×10^{-1}	1.25×10^{-2}	2.59×10^{-3}	2.97×10^{-3}
Isotherm of Temkin							
100°	6.18×10^{-1}	5.39×10^{-3}	1.32×10^{-4}	3.25×10^{-4}	3.18×10^{-3}	1.35×10^{-7}	2.62×10^{-6}
200°	2.05×10^{-2}	4.88×10^{-2}	1.82×10^{-3}	2.16×10^{-3}	8.36×10^{-6}	2.00×10^{-5}	1.59×10^{-3}

variation of the heat of adsorption with several other parameters, the ammonia adsorption centers appear very likely to be nonuniform on sodium-silica catalysts, especially on sodium-rich ones.

The results of the present investigations indicate that both the number and the nature of ammonia adsorption centers are related to the surface sodium content, experimental temperature, and ammonia pressure. The increase in the heat of adsorption with rise in temperature may be explicable in terms of formation of new ammonia adsorption centers. This phenomenon is believed to be associated with the

reversible cleavage of the hydrogen bonds between adjacent OH or OH and ONa groups, which has been partially confirmed by IR spectral evidence.

Another method for studying the nature of acidic centers on the surface of sodium-silica catalysts involved the examination of the kinetics of ammonia adsorption. The rate of adsorption was measured at temperatures of 100° and 200°C. The kinetic data were found to be consistent with the Elovich, rather than with the Langmuir, equation. The rate of adsorption is presented in Figs. 23 and 24 as a function of the logarithm of time. The linear relation

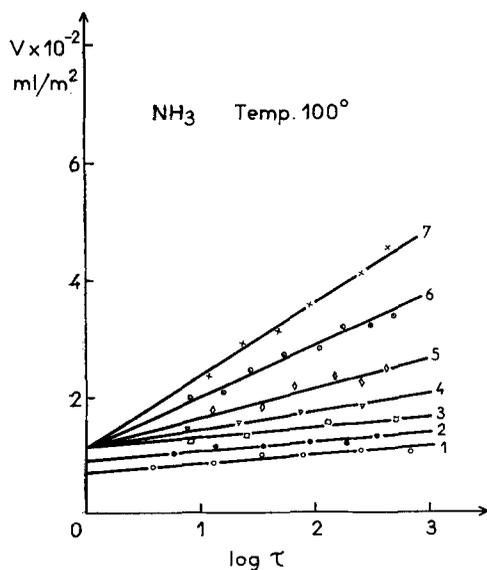


FIG. 23. The rate of ammonia adsorption as a function of time

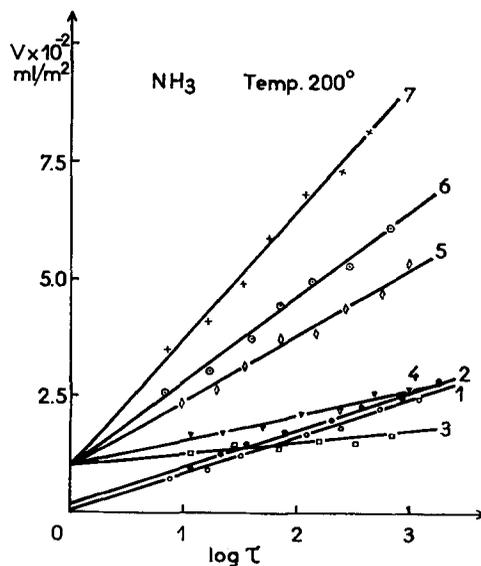


FIG. 24. The rate of ammonia adsorption as a function of time.

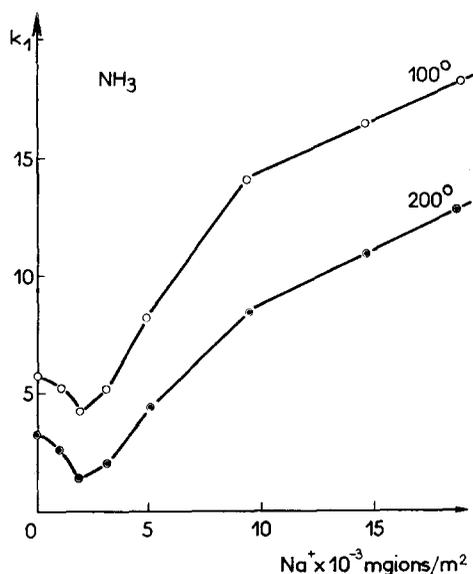


FIG. 25. The kinetics of ammonia adsorption Elovich function K_1 vs. mg-ions Na^+/m^2 .

obtained proves the Elovich (10) kinetic equation to be a good fit and shows the ammonia adsorption centers to be nonuniform.

The Elovich equation was used in the integrated form:

$$V = \frac{1}{b} \ln(\tau - \tau_0) + \frac{1}{b} \ln ab,$$

where V is the volume of the gas adsorbed in time τ : $\tau_0 = 1/ab$; a , constant; and b , constant.

Since in the prevailing conditions τ_0 is very low, it was neglected and the equation reduced to the form

$$v = k_1 \log \tau + k_2,$$

where $k_1 = 2.303/b$ and $k_2 = 2.303/b \log ab$.

A linear plot of V vs. $\log \tau$ was used for determination of coefficients k_1 and k_2 , whereupon τ_0 was evaluated from the formula $k_2/k_1 = \log \tau_0$. The values of k_1 and τ_0 are presented graphically as functions of Na^+ mg-ions per square meter of the catalyst surface area (Figs. 25 and 26). As the coefficient of the logarithm of time, the constant k_1 characterizes the net rate of adsorption of ammonia, whereas the

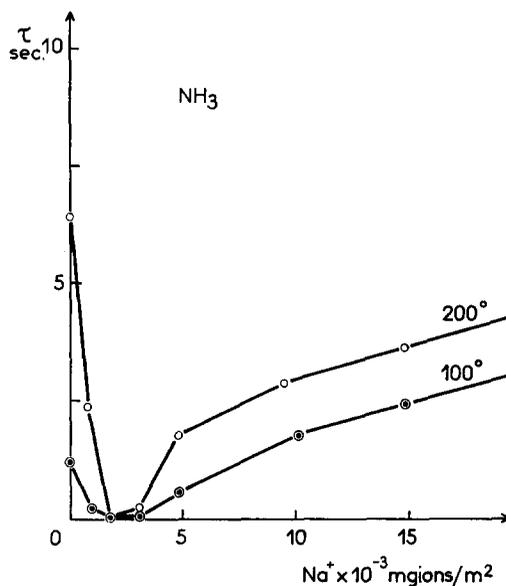


FIG. 26. The kinetics of ammonia adsorption. Elovich function ξ_0 sek. w s mg-ions Na^+/m^2 .

constant τ_0 defines the induction time of the surface reaction.

The curves in Figs. 25, 26 initially fall down, then pass through minima and rise. The minima occur at 2.5×10^{-3} mg-ions of Na^+/m^2 . These curves demonstrate that the kinetics of ammonia adsorption is highly affected by the sodium content in the silica surface.

In spite of the accidental agreement with the Langmuir isotherm, the present data show that the ammonia adsorption centers are nonuniform on the surface of the catalysts studied. According to the sodium content and experimental temperature, the adsorption of ammonia undergoes modifications suggestive of changes in both the thermodynamics and kinetics of the process.

The observed and the calculated data disclose two distinct features, viz., the occurrence of rapid changes and the presence of extrema. The number of mg-ions of sodium ($0.5-1.5 \times 10^{-3}$ mg-ions Na^+/m^2) at which the rapid changes—confirmed also by Uytterhoeven—occur, may be attributed to the limiting sodium content in the silica catalyst, which results in “rapid” surface structural changes. The adsorption-

related curves show minima, maxima and inflection points which are attributed to changes in the acid properties of the catalyst surface. This phenomenon may be explained in terms of structural changes in, as also associated with the sodium hydroxide impregnation of, the catalyst surface. Initially, on treatment with diluted sodium hydroxide solutions, the hydrogens of surface silanol groups are being replaced by sodium ions, the oxygen-silicon bonds being only slightly or not affected at all. As the sodium ion concentration in the solution is increased, both phenomena can occur simultaneously; above a certain concentration the Si-O bonds will be rapidly ruptured and -Si-OH and -Si-ONa groupings will be formed which constitute adsorption centers for ammonia and pyridine bases. This interpretation holds as long as at higher sodium ion concentrations the rupture of Si-O bonds and formation of

$$\begin{array}{c} | \\ \text{—Si—ONa} \end{array} \text{ and } \begin{array}{c} | \\ \text{—Si—OH} \end{array}$$
 groupings proceed faster than does the replacement of the silanol hydrogen ion by the sodium ion.

When seen from a more general point of view, the above results show that poisoning of acid catalysts by alkali-metal ions constitutes a very complicated process. While poisoning the acidic centers of one

type, the alkali-metal ions give rise to the formation of other types of acidic centers. These new centers are very likely to exhibit a catalytic activity different from that of the centers occurring in unalkalized catalysts. Such alterations are indicated by changes in the quantities associated with the thermodynamics and kinetics of ammonia adsorption on sodium-silica catalysts as compared with the values recorded for pure silica.

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